

▲ FIGURE 31.1 Flow chart for group separation.

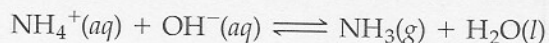
To derive the maximum benefit from this exercise, you should be thoroughly familiar with the group-separation chart in Figure 31.1. You should know not only which 10 cations (by formula and charge) you are studying but also how they are separated into groups. More details regarding the identification of these cations are provided in the flow chart for cations (Figure 31.2) and in the following discussion about the chemistry of the analytical scheme. Make frequent referrals to the flow charts while learning about the chemistry of the qualitative analysis scheme.

1 Detection of Sodium and Ammonium

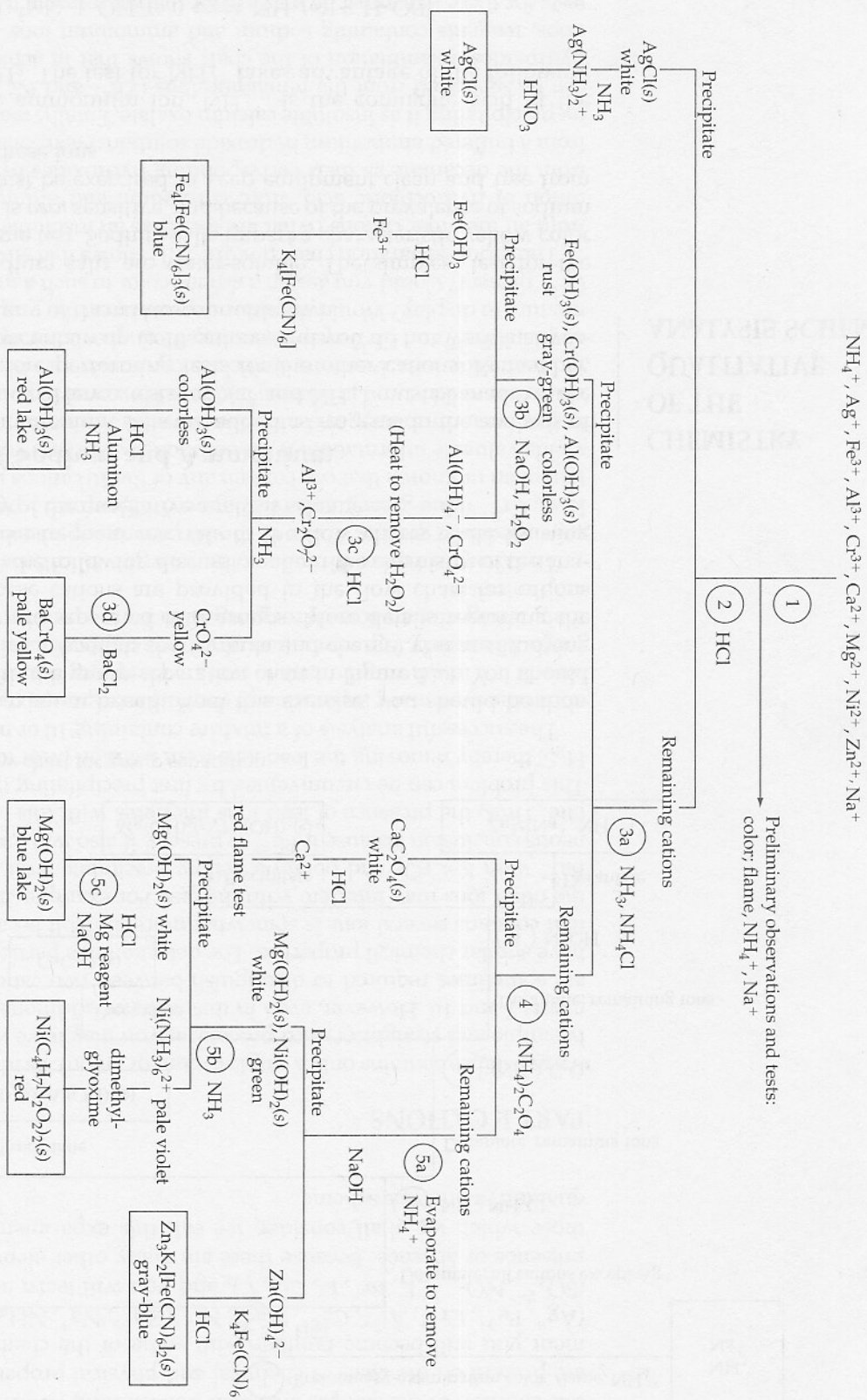
Sodium salts and ammonium salts are added as reagents in the analysis of your general unknown. Hence, tests for Na^+ and NH_4^+ must be made on the original sample before performing tests for the other cations. Remember, your unknown may contain up to 10 cations, and you do not want inadvertently to introduce any of them into your unknown.

Sodium Most sodium salts are water-soluble. The simplest test for the sodium ion is a flame test. Sodium salts impart a characteristic yellow color to a flame. The test is *very* sensitive, and because of the prevalence of sodium ions, much care must be exercised to keep equipment clean and free from contamination by these ions.

Ammonium The ammonium ion, NH_4^+ , is the conjugate acid of the base ammonia, NH_3 . The test for NH_4^+ takes advantage of the following equilibrium:



CHEMISTRY OF THE QUALITATIVE ANALYSIS SCHEME

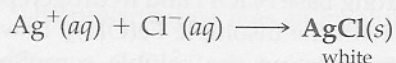


▲ FIGURE 31.2 Cation flow chart.

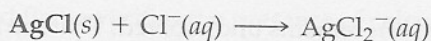
Thus, when a strong base such as sodium hydroxide is added to a solution of an ammonium salt, and this solution is heated, NH_3 gas is evolved. The NH_3 gas can easily be detected by its effect upon moist red litmus paper.

2 Separation and Detection of Silver

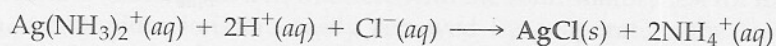
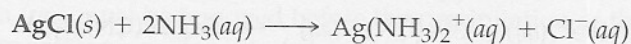
All chloride salts are soluble in water except those of Pb^{2+} , Hg_2^{2+} , and Ag^+ . Silver can be precipitated and separated from the other nine cations that we are considering by the addition of HCl to the original unknown:



A slight excess of HCl is used to ensure the complete precipitation of silver ions and to reduce their solubility by the common-ion effect; an excess of chloride ions drives the above equilibrium to the right. However, a large excess of chloride ions must be avoided because AgCl tends to dissolve by forming a *soluble-complex ion*:



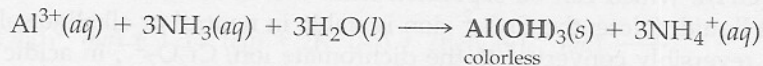
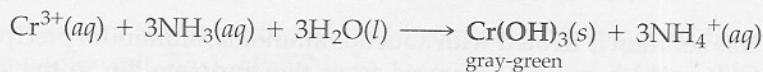
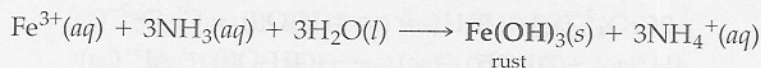
To be absolutely certain that the white precipitate is AgCl (PbCl_2 and Hg_2Cl_2 are also insoluble, and they are also white), NH_3 is added to the precipitate. If the precipitate is indeed AgCl , it will dissolve and then re-precipitate when the ammoniacal solution is made acidic:



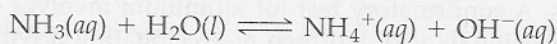
The other two insoluble chlorides do not behave this way. Thus we can be assured that the white chloride precipitate is silver chloride.

3a Separation and Detection of Iron, Aluminum, and Chromium

Iron, aluminum, and chromium can be separated from the other ions (Ca^{2+} , Mg^{2+} , Ni^{2+} , and Zn^{2+}) by making the solution alkaline and precipitating these cations as their corresponding hydroxides:



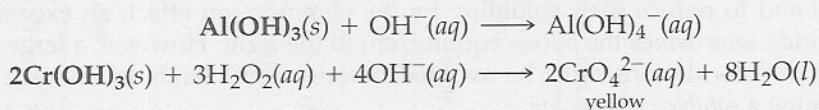
The hydroxide-ion concentration required to precipitate these three ions must be carefully controlled, because if it is too high, $\text{Mg}(\text{OH})_2$ will also precipitate. An alkaline buffer of NH_3 and NH_4Cl provides a hydroxide-ion concentration that is high enough to precipitate Fe^{3+} , Cr^{3+} , and Al^{3+} and yet is low enough to prevent precipitation of $\text{Mg}(\text{OH})_2$. Aqueous ammonia is a weak base:



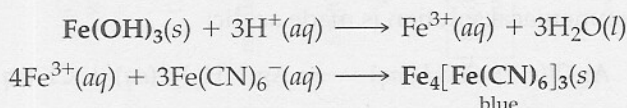
By itself, it would provide too high of a hydroxide-ion concentration, and $\text{Mg}(\text{OH})_2$ would precipitate along with the other cations. However, the NH_4^+ ions derived from the NH_4Cl causes this equilibrium to shift to the left; this reduces the hydroxide-ion concentration sufficiently to prevent Mg^{2+} from precipitating.

3b Separation and Detection of Iron

Iron hydroxide can be separated from the other hydroxides by treating the precipitate with the strong base NaOH and hydrogen peroxide, H_2O_2 . These reagents do not react with the insoluble $\text{Fe}(\text{OH})_3$; however, $\text{Al}(\text{OH})_3$ is amphoteric and dissolves, forming the soluble complex ion $\text{Al}(\text{OH})_4^-$. The $\text{Cr}(\text{OH})_3$ also dissolves, being oxidized by H_2O_2 to form CrO_4^{2-} :

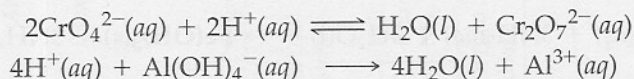


The rust-colored $\text{Fe}(\text{OH})_3$ remains undissolved. That the rust-colored precipitate is in fact iron hydroxide can be confirmed by dissolving it in acid and then adding potassium hexacyanoferrate(II), $\text{K}_4[\text{Fe}(\text{CN})_6]$, and noting the formation of a dark blue precipitate (Prussian blue):

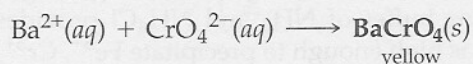


3c and 3d Separation and Detection of Chromium and Aluminum

While iron was being precipitated as the hydroxide, chromium was oxidized to the yellow chromate ion, CrO_4^{2-} , and aluminum was converted to the soluble complex aluminate ion, $\text{Al}(\text{OH})_4^-$, which is colorless. These two ions are in the supernatant liquid, which upon acidification converts the chromate ion to the orange dichromate ion and the aluminate to the colorless solvated aluminum ion:

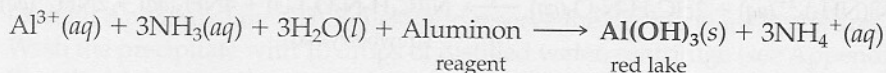


When this solution is treated with aqueous ammonia, aluminum precipitates as $\text{Al}(\text{OH})_3$, which can be separated from the chromate ion in the supernatant liquid. (Note: the CrO_4^{2-} ion is stable in neutral or alkaline solution but is reversibly converted to the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, in acidic solution.) The formation of a yellow precipitate, BaCrO_4 , upon the addition of barium chloride, confirms the presence of chromium:



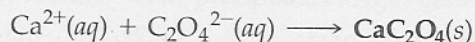
Aluminum hydroxide is a clear, colorless substance and is difficult to see in this analysis. A confirmatory test for aluminum involves dissolving the aluminum hydroxide in acid and then re-precipitating it with ammonia in

the presence of Aluminon reagent. As the aluminum hydroxide precipitates, it absorbs the Aluminon reagent and assumes a red coloration known as a "lake."

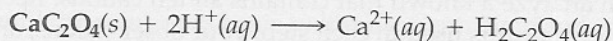


4 Separation and Detection of Calcium

Calcium Calcium can be separated from the remaining cations (Mg^{2+} , Ni^{2+} , and Zn^{2+}) by precipitating it as an insoluble oxalate salt:



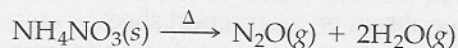
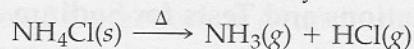
If magnesium is present, it is possible that it will precipitate and be mistaken for calcium. To confirm that the precipitate is that of calcium and not magnesium, it is dissolved in acid and a flame test is performed on the solution.



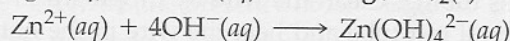
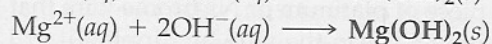
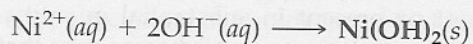
A transient brick-red flame verifies the presence of calcium ions. Magnesium ions do not impart any color to a flame.

5a Separation and Detection of Zinc

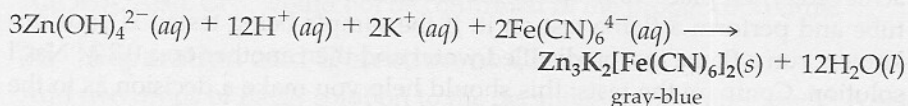
Separation of zinc from magnesium and nickel can be accomplished by precipitating $\text{Mg}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ from a strongly alkaline solution. Excess ammonium ions must be removed before the precipitation of these hydroxides because ammonium ions interfere with the confirmatory test for magnesium. Ammonium ions are easily removed by evaporating the solution, which has been acidified with nitric acid to dryness:



Although magnesium and nickel form insoluble hydroxides in the presence of a strong base, zinc is amphoteric and forms the soluble complex ion $\text{Zn}(\text{OH})_4^{2-}$:

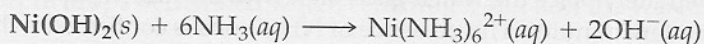


The presence of zinc is confirmed by precipitating it from an acidic solution as a gray-blue salt, $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$:

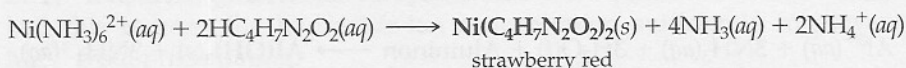


5b Separation and Detection of Nickel

Because nickel forms the soluble complex ion hexaamminenickel(II), $\text{Ni}(\text{NH}_3)_6^{2+}$, in the presence of aqueous ammonia, it can be separated from $\text{Mg}(\text{OH})_2$:

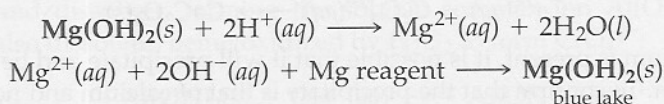


It is confirmed by forming a strawberry red precipitate, $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$, with an organic reagent, dimethylglyoxime.



5c Detection of Magnesium

Magnesium is confirmed by dissolving the hydroxide with acid and then reprecipitating it in the presence of an organic compound called "Magnesium reagent." The presence of Mg^{2+} is indicated by formation of a blue lake.



PROCEDURE

First you will analyze a known that contains all ten cations. Record on your report sheet the reagents used in each step, your observations, and the equations for each precipitation reaction. After completing this practice analysis, obtain an unknown. Follow the same procedures as with the known, again recording reagents and observations. Also record conclusions regarding the presence or absence of all cations. *Before beginning this experiment, review the techniques used in qualitative analysis found in Appendix I: heating solutions, precipitation, centrifugation, washing precipitates, and testing acidity.*

Waste Disposal Instructions All waste from this experiment should be placed in appropriate containers in the laboratory.

1 Initial Observations and Tests for Sodium and Ammonium

Note the color of your sample and record any conclusions about what cations are present or absent on your report sheet.

The flame test for sodium is very sensitive, and traces of sodium ion will impart a characteristic yellow color to the flame. Just about every solution has a trace of sodium and thus will give a positive result. On the basis of the intensity and duration of the yellow color, you can decide whether Na^+ is merely a contaminant or present in substantial quantity. To perform the flame test, obtain a piece of platinum or Nichrome wire that has been sealed in a piece of glass tubing. Clean the wire by dipping it in 12 M HCl that is contained in a small test tube and heat the wire in the hottest part of your Bunsen burner flame. Repeat this operation until no color is seen when the wire is placed in the flame. Several cleanings will be required before this is achieved. Then place 10 drops of the solution to be analyzed in a clean test tube and perform a flame test on it. If the sample being tested is your unknown, run a flame test on distilled water and then another on a 0.2 M NaCl solution. Compare the tests; this should help you make a decision as to the presence of sodium in your unknown.

Place 10 drops of the original sample to be analyzed in an evaporating dish or a crucible. Moisten a strip of red or neutral litmus paper with distilled water and place the paper on the bottom of a small watch glass. Add 10 drops of 3 M NaOH to the unknown, swirl the evaporating dish or crucible, and immediately place the watch glass on it with the litmus paper down. Let stand for a few minutes. The presence of NH_4^+ ions is confirmed if the paper turns blue.

2 Separation and Detection of Silver

Place 10 drops of the original solution to be analyzed in a small test tube, add five drops of distilled water, and two drops of 6 M HCl. Stir well, centrifuge (consult Appendix I for techniques), and reserve the decantate for Procedure 3. Wash the precipitate with 10 drops of distilled water, centrifuge (see Appendix I), and add the washings to the decantate. Dissolve the precipitate in four drops of 6 M NH_3 ;^{*} then add 6 M HNO_3 to the ammoniacal solution until it is acidic to litmus. (**CAUTION: nitric acid can cause severe burns: Avoid contact with it. If you come in contact with it, immediately wash the area with copious amounts of water**) A curdy white precipitate of AgCl confirms the presence of Ag^+ ions.

3a Separation and Detection of Iron, Aluminum, and Chromium

To the decantate from Procedure 2 add two drops of NH_4Cl solution and 6 M NH_3 until the solution is basic to litmus. Centrifuge and reserve the decantate for Procedure 4. Wash the precipitate with 10 drops of distilled water, centrifuge, and add the washings to the decantate.

3b Separation and Detection of Iron

To the precipitate from Procedure 3a, add five drops of distilled water, 10 drops of 3 M NaOH, and five drops of 3% H_2O_2 . Stir well, centrifuge, and reserve the decantate for Procedure 3c. Wash the precipitate with 10 drops of distilled water and add the washings to the decantate. Dissolve the reddish-brown precipitate in two drops of 6 M HCl and add 10 drops of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. A blue precipitate of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ confirms the presence of Fe^{3+} ions.

3c Separation and Detection of Aluminum

If the decantate from Procedure 3b is yellow in color, place it in an evaporating dish or a crucible and evaporate almost to dryness to remove excess H_2O_2 (see Note 1 below). Add 10 drops of distilled water and 6 M HCl until acid to litmus. Then add 6 M NH_3 until the solution is basic to litmus. Centrifuge and reserve the decantate for Procedure 3d. Wash the precipitate with 10 drops of distilled water, centrifuge, and add the washings to the decantate. Dissolve the precipitate in two drops of 6 M HCl, add two drops of Aluminon reagent, and 6 M NH_3 until basic to litmus. Centrifuge the solution. A red "lake" confirms the presence of Al^{3+} ions.

Note 1 Hydrogen peroxide is a reducing agent in acid solutions, so CrO_4^{2-} ions could be reduced to Cr^{3+} when the solution is acidified. When NH_3 is added, $\text{Cr}(\text{OH})_3$ will be precipitated and could be incorrectly reported as $\text{Al}(\text{OH})_3$. Also, Cr^{3+} would not be confirmed in the proper procedure.

3d Separation and Detection of Chromium

Add two drops of BaCl_2 solution to the decantate from Procedure 3c. A yellow precipitate of BaCrO_4 confirms the presence of Cr^{3+} ions.

4 Separation and Detection of Calcium

Add three drops of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution to the decantate from Procedure 3a and centrifuge. Reserve the decantate for Procedure 5a. Wash the precipitate with 10 drops of distilled water, centrifuge, and add the washings to the

^{*}Bottles may be labeled 6 M NH_4OH .

decantate. Dissolve the precipitate of CaC_2O_4 in two drops of 6 M HCl and carry out a flame test with the solution. A brick-red flame confirms Ca^{2+} ions (see Note 2 below).

Note 2 If magnesium ions are present, they may be precipitated as MgC_2O_4 .

To determine if MgC_2O_4 is precipitated, test the acid solution for Mg^{2+} as described in Procedure 5c.

5a Separation and Detection of Zinc

Place the decantate from Procedure 4 in an evaporating dish and carefully evaporate to dryness using a burner flame. (**CAUTION: Concentrated HNO_3 can cause severe burns: Avoid contact with it. If you come in contact with it, immediately wash the area with copious amounts of water.**) Add five to six drops of 16 M HNO_3 and heat again until no more fumes are observed (you are removing excess NH_4^+ ions that would interfere with the tests for Mg^{2+} ions). Dissolve the residue in five drops of 6 M HCl. Add 10 drops of distilled water to the HCl solution and transfer it to a small test tube. Wash out the evaporating dish with 10 drops of distilled water, and add the wash to the acid solution. Add 3 M NaOH until the solution is basic to litmus; centrifuge, and reserve the precipitate for Procedure 5b. Wash the precipitate with 10 drops of distilled water and add the washings to the decantate. Add three drops of $\text{K}_4[\text{Fe}(\text{CN})_6]$ to the decantate and acidify with 6 M HCl; a gray-blue coloration or precipitate of $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ confirms the presence of Zn^{2+} ions.

5b Separation and Detection of Nickel

(**Caution: Concentrated NH_3 has a strong irritating odor and causes severe burns: Avoid inhaling it. If you come in contact with it, immediately wash the area with copious amounts of water.**)

Add five drops of distilled water and five drops of 15 M NH_3 to the precipitate from Procedure 5a; centrifuge, and reserve the precipitate for Procedure 5c. Wash the precipitate with 10 drops of distilled water, and add the wash to the decantate. Add one drop of dimethylglyoxime solution to the decantate; a strawberry-red precipitate of $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$ confirms the presence of Ni^{2+} ions.

5c Detection of Magnesium

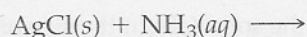
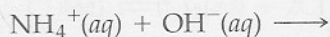
If Ni^{2+} ions were confirmed in Procedure 5b, add 15 M NH_3 to the precipitate saved from Procedure 5b until a negative result for Ni^{2+} is obtained. Dissolve the hydroxide precipitate in two drops of 6 M HCl; add two drops of "Magnesium reagent" and 3 M NaOH until the solution is basic. A blue lake confirms the presence of Mg^{2+} ions.

PRE LAB QUESTIONS

Before beginning Part I of this experiment in the laboratory, you should be able to answer the following questions:

1. What are the names and formulas of the 10 cations you will identify?
2. Why are confirmatory tests necessary in identifying ions?
3. Which of the 10 cations are colored, and what are their colors?
4. Which salt is insoluble: FeCl_3 , ZnCl_2 , NaCl , or AgCl ?
5. How could you separate Fe^{3+} from Ag^+ ?
6. How could you separate Cr^{3+} from Mg^{2+} ?

7. How could you separate Al^{3+} from Ag^+ ?
 8. Complete and balance the following:



PART II: ANIONS

A systematic scheme based on the kinds of principles involved in cation analysis can be designed for the analysis of anions. Because we shall limit our consideration to only six anions (SO_4^{2-} , NO_3^- , Cl^- , Br^- , I^- , and CO_3^{2-}) and will not consider mixtures of the ions, our method of analysis is quite simple and straightforward. It is based on specific tests for the individual ions and does not require special precaution to eliminate interferences that may arise in mixtures.

Initially you will make a general test on a solid salt with concentrated sulfuric acid (H_2SO_4). The results of this test should strongly suggest what the anion is. You will then confirm your suspicions by performing a specific test for the ion you believe to be present.

Table 31.1 summarizes the behavior of anions (as dry salts) with concentrated sulfuric acid.

Perform the general sulfuric acid test described below on the individual anions. Then perform the specific tests on each of the ions. Record your

DISCUSSION

PROCEDURE

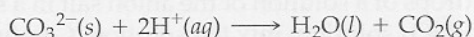
TABLE 31.1 Behavior of Anions with Concentrated Sulfuric Acid, H_2SO_4

A. Cold H_2SO_4

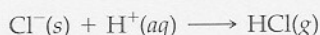
SO_4^{2-} No reaction.

NO_3^- No reaction.

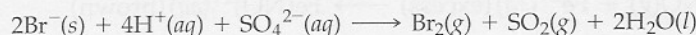
CO_3^{2-} A colorless, odorless gas forms.



Cl^- A colorless gas forms. It has a sharp-pungent odor, gives an acidic test result with litmus, and fumes in moist air.

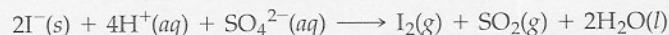


Br^- A brownish-red gas forms. It has a sharp odor, gives an acidic test result with litmus, and fumes in moist air. The odor of SO_2 may be detected.



(HBr is also liberated)

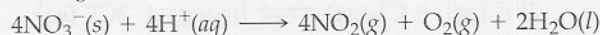
I^- Solid turns dark brown immediately with the slight formation of violet fumes. The gas has the odor of rotten eggs, gives an acidic test result with litmus, and fumes in moist air.



(HI and H_2S are also liberated)

B. Hot Concentrated H_2SO_4

There are no additional reactions with any of the anions except NO_3^- , which forms brown fumes of NO_2 gas.



observations and equations for the reactions that occur. After completing these tests on the six anions, obtain a solid salt unknown and identify its anion. Record your observations and conclusion. Only one anion is present in the salt.

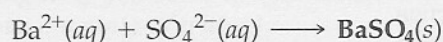
Sulfuric Acid Test

Place a small amount of the solid (about the size of a pea) in a small test tube. Add one or two drops of 18 M H_2SO_4 and observe everything that occurs, especially the color and odor of gas formed. (CAUTION: Concentrated H_2SO_4 causes severe burns. Do not get it on your skin or clothing. If you come in contact with it, immediately wash the area with copious amounts of water.) DO NOT place your nose directly over the mouth of the test tube, but carefully fan gases toward your nose. Then carefully heat the test tube, but not so strongly as to boil the H_2SO_4 . (CAUTION: If you heat the acid too strongly, it could come shooting out!) Note whether or not brown fumes of NO_2 are produced. (CAUTION: Do not look down into the test tube. Do not point the test tube at yourself or at your neighbors. SAFETY GLASSES MUST BE WORN.)

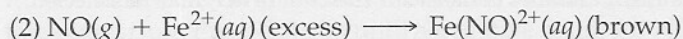
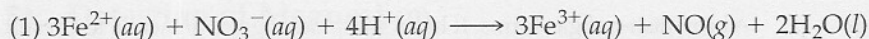
Specific Tests for Anions

When an anion is indicated by the preliminary test result with concentrated H_2SO_4 , it is confirmed using the appropriate specific test. Make an aqueous solution of the solid unknown and perform the following tests on portions of this solution.

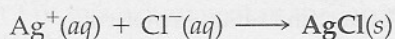
Sulfate Place 10 drops of a solution of the anion salt in a test tube, acidify with 6 M HCl , and add a drop of BaCl_2 solution. The formation of a white precipitate of BaSO_4 confirms SO_4^{2-} ions.



Nitrate Place 10 drops of a solution of the anion salt in a small test tube and add five drops of FeSO_4 solution; mix the solution. Carefully, without agitation, pour concentrated H_2SO_4 down the inside of the test tube so as to form two layers. The formation of a brown ring between the two layers confirms NO_3^- ions.



Chloride Place 10 drops of a solution of the anion salt in a test tube and add a drop of AgNO_3 solution. A white, curdy precipitate confirms Cl^- ions.



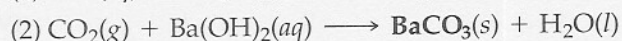
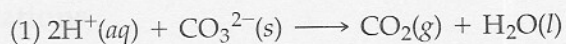
Bromide Place 10 drops of a solution of the anion salt in a test tube, add three drops of 6 M HCl , then add five drops of Cl_2 water and five drops of mineral oil. Shake well. Br^- ions are confirmed if the mineral-oil (top) layer is colored orange to brown. Wait 30 s for the layers to separate.



Iodide Repeat the test as described for Br^- ions. If the mineral-oil layer is colored violet, I^- ions are confirmed.



Carbonate Place a small amount of the solid anion salt in a small test tube and add a few drops of 6 M H_2SO_4 . If a colorless, odorless gas evolves, hold a drop of $\text{Ba}(\text{OH})_2$ solution over the mouth of the test tube using either an eyedropper or Nichrome wire loop; CO_3^{2-} ions are confirmed if the drop turns milky.



Before beginning Part II of this experiment in the laboratory, you should be able to answer the following questions:

PRE LAB QUESTIONS

1. Give the names and formulas of the anions to be identified.
2. Describe the behavior of each solid containing the anions toward concentrated H_2SO_4 .
3. If you had a mixture of NaCl and Na_2CO_3 , would the action of concentrated H_2SO_4 allow you to decide that both Cl^- and CO_3^{2-} were present?